

# PATENT SPECIFICATION

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## (54) SHAMPOO COMPOSITIONS

(71) We, NATIONAL STARCH AND CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 10 Funderne Avenue, Bridgewater, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention is directed to conditioning shampoo formulations prepared from specific cationic polymers, anionic surfactants and optional nonionic surfactants. The resultant shampoo formulations are economical to prepare, exhibit improved lathering and possess commercially acceptable conditioning properties.

The need for a shampoo formulation which conditions (i.e. renders the hair more manageable) as it cleans has long been recognized in the art. Thus, while conditioning agents for application to already shampooed hair have long been known, it has only been within recent years that conditioning shampoos have become available. A number of these shampoos are specially formulated for mildness and hence, low detergency, so as to leave a portion of the hair's natural oils behind. Consequently the hair soon looks and feels greasy and dirty. Other formulations contain certain oily components, such as polyglycols, fatty acid esters of glycols, natural or synthetic waxes or lanolin derivatives, which components are deposited on the hair during shampooing. The oily nature of such components, however, inhibits lathering of the shampoo and also contributes to the feeling of greasy, dirty hair soon after shampooing.

A third type of conditioning shampoo contains a cationic polymer which can deposit on the hair during shampooing to impart the desired degree of manageability while overcoming the previously described problem of greasiness development. The primary difficulty encountered in preparing such shampoo conditioners has been that of achieving a stable system without destroying the delicate balance of conditioning and other functional properties. Previous attempts to provide solubility of the conditioning polymer while achieving suitable cleaning and lathering as well as deposition of the polymer on the hair have resulted in the finding that specific polymers when incorporated with amphoteric surfactants (detergents), optionally in the presence of nonionic or ionic surfactants, will result in shampoo formulations which condition as they clean. Such findings are due to the superior compatibility of the amphoterics with the commonly used cationic polymers thereby allowing maximum deposition of the polymer onto the hair during shampooing.

Thus, U.S. Patent 4,009,256 discloses a conditioning shampoo comprising an aqueous solution of (1) a cationic polymer which is a water-soluble acid salt of an aminoalkyl ester of a carboxylic acid polymer, (2) an amphoteric detergent, and (3) optionally, at least one nonionic surfactant or at least one ionic surfactant or a combination thereof, wherein any plurality of ionic surfactants utilized consists of those of the same ionogenic class. The necessity for employing the amphoteric detergent in such formulations is supported and reinforced by substantially all the patents directed to conditioning shampoos. Thus, U.S.

Patents 3,313,734; 3,962,418; 2,999,069; 3,055,836; 3,996,146 and 3,400,198, among others, require the presence of an amphoteric or polar non-ionic component in order that the conditioning polymer be compatible with the remaining ingredients in the shampoo formulation. Of all the pertinent art known to applicants, only U.S. Patent 3,816,616 discloses a conditioning shampoo which does not require the presence of a compatibilizing agent and such teaching is directed only to the use of one very specific cationic polymer -- a quaternized modified cellulosic polymer.

The primary disadvantages to the requirement for an amphoteric detergent or surfactant to be present in conditioning shampoo formulations are related to their high cost and weak foaming ability relative to the anionic surfactants available. Thus the use of amphoteric surfactants substantially increases the cost of producing conditioning shampoos, thereby limiting the consumer market to which the products may be directed.

In accordance with the present invention there is provided a conditioning shampoo free of amphoteric surfactants and consisting essentially of water and

(1) from 0.1 to 10.0%, by weight of the total solution, of a water-soluble acid salt of an aminoalkyl ester of a cationic polymer having a molecular weight of 5,000 to 250,000;

(2) from 5.0 to 30.0%, by weight active solids based on the weight of the total solution, of selected anionic surfactant as hereinafter defined; and

(3) from 0 to 10.0%, by weight active solids based on the weight of the total solution of at least one nonionic surfactant.

When used in the usual and conventional manner in shampooing hair, the resultant shampoos of the described formulation exhibit both cleaning and conditioning properties. Moreover, due to the relatively high level of anionic surfactant present in the formulations, these novel shampoos are characterized by superior lathering, an attribute widely desired in the consumer marketplace.

The cationic polymers useful in the conditioning shampoos of the present invention are those employed in U.S. Patent 4,009,256 to which reference should be made. Specific and preferred examples of cationic polymers disclosed therein and useful in the present invention are mineral acid salts of amino-alkyl esters of homo- and copolymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, for example, acrylic acid, methacrylic acid, crotonic acid, ethacrylic acid, fumaric acid, maleic acid and itaconic acid, and the aminoalkyl groups containing from 2 to 6 carbon atoms. Useful aminoalkyl groups include, for example, aminoethyl, N-methyl aminoethyl, N-ethyl aminoethyl, 2-aminopropyl and t-butyl aminoethyl, with the aminoethyl being preferred.

More specifically, the useful polymers include the salts of the aminoalkyl esters of (a) homopolymers of homopolymerizable unsaturated carboxylic acids having 3 to 5 carbon atoms; (b) copolymers of copolymerizable mixtures of acids, and (c) copolymers formed of unsaturated carboxylic acids having 3 to 5 carbon atoms and at least one copolymerizable ethylenically unsaturated comonomer selected from the group consisting of vinyl acetate and vinyl propionate; vinyl methyl ether and vinyl ethyl ether; the  $C_1$ - $C_{18}$  alkyl half esters of maleic and fumaric acids, for example, diethyl furmarate, dioctyl furmarate, dibutyl maleate, dioctyl maleate, monobutyl maleate, monomethyl fumarate, and monoethyl fumarate; amides of acrylic and methacrylic acids, for example, acrylamide, N-methyl acrylamide, and methacrylamide; and the  $C_1$ - $C_{18}$  alkyl and  $C_2$ - $C_4$  hydroxyalkyl esters of acrylic and methacrylic acids. Specific examples of the latter class of comonomers includes methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, dodecyl acrylate, stearyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, as well as the corresponding methacrylate esters. Preferred comonomers include in the amides and the  $C_1$ - $C_{18}$  alkyl and  $C_2$ - $C_4$  hydroxyalkyl esters of acrylic and methacrylic acids.

It will be recognized that, for the purposes of the present invention, the copolymeric mixture of copolymerizable carboxylic acids of group (b) may contain the various monomeric components in any proportion. However, in the case of the copolymers of group (c), there must be present at least 50 mole percent, and preferably 75 mole percent, of the unsaturated carboxylic acid component.

Particularly preferred cationic polymers for use herein are the phosphate salts of poly(aminoethyl acrylate) or poly(aminoethyl acrylate hydroxypropyl acrylate) or a terpolymer of an aminoalkyl ester of an ethylenically unsaturated carboxylic acid, an amide of an ethylenically unsaturated carboxylic acid, and a hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid wherein said cationic polymer has a molecular weight between 25,000 and 100,000.

With regard to the preparation of cationic polymers useful in the practice of this invention, the practitioner will recognize that such materials may be commercially available or may normally be synthesized either (1) by polymerizing monomers which have the functional aminoalkyl ester groups attached or (2) by subsequently affixing said groups to a base polymer such as the homopolymer of an ethylenically unsaturated carboxylic acid or a

copolymer formed with at least one ethylenically unsaturated carboxylic acid and one or more copolymerizable comonomers. For example, the first method would typically involve the homopolymerization of one of the following: t-butylaminoethyl methacrylate dimethylaminoethyl methacrylate, or the copolymerization of any one of the foregoing compounds with one or more of the above-mentioned copolymerizable comonomers. Such methods are disclosed in, inter alia, U.S. Patent No. 2,979,491, U.S. Patent No. 2,744,884, and in U.S. Patent No. 2,625,471. The second method wherein the functional aminoalkyl ester groups are affixed to the base polymer may be carried out according to the process taught in, inter alia, U.S. Patent No. 3,372,149. Regardless of the means of synthesis selected, a well known free radical polymerization procedure is usually entailed. These compounds, upon utilization in accordance with this invention, are all characterized by their ability to display the desirable hair conditioning properties.

The selected anionic surfactants employed in the present shampoo compositions are also discussed in U.S. Patent 4,009,256 and are specifically one or more of the following: a fatty alcohol sulfate or ether sulfate such as sodium lauryl sulfate, triethanolamine lauryl sulfate or sodium lauryl ether sulfate; an alkylaryl sulfonate, e.g. sodium or potassium isopropylbenzene sulfonate or isopropyl naphthalene sulfonate; an alkali metal alkyl sulfosuccinate, e.g. sodium octenyl sulfosuccinate, sodium N-methyl-N-palmitoyl-taurate, sodium oleyl isethionate; a fatty alcohol ether sulfosuccinate; an alkali metal salt of a sulfosuccinate half ester of an alkanolamide; or an alkali metal salt of an alkylarylpolylethoxyethanol sulfate or sulfonate, e.g., a sodium t-octylphenoxypolyethoxyethyl sulfate or sulfonate having from 1 to 5 oxyethylene units.

If desired, various nonionic surfactants may also be employed including the polyoxyalkylene alkyl ethers and condensates of alkylene oxides with fatty acids. With regard to proportions, these novel conditioning shampoos generally contain from 0.1 - 10.0%, preferably 0.5 to 2.0% by weight of the total solution of the cationic polymer, 5.0 to 30.0%, preferably 10.0 to 20.0%, by weight of the total solution of the anionic surfactant and 0 to 10.0%, preferably 2.0 to 8.0%, by weight of the total solution of the nonionic surfactant.

The practitioner will recognize that the actual concentration of any particular cationic polymer used in a given conditioning shampoo preparation encompassed within this invention may vary within the prescribed range, for many reasons. For example, the maximum usable concentration will depend on the nature and molecular weight of the polymer, its compatibility with the particular surfactant employed and any optional ingredients used, the degree of pH adjustment, if required, and the neutralizing agent utilized.

Since some of the ingredients employed in the practice of this invention tend to support bacterial growth, a small amount of a preservative should be added to prevent such microbial growth. Though other well known preservatives and bactericides such as formaldehyde may be employed, we prefer to use the lower molecular weight alkyl p-hydroxybenzoates.

Optional ingredients, in addition to the nonionic surfactant described hereinabove, may be incorporated into the conditioning shampoo compositions of this invention in order to modify certain properties thereof. Among these additives may be included: emollients and lubricants such as glycols, esters, and glycerine; lanolin compounds; protein hydrolyzates and other protein derivatives, ethylene oxide adducts, and cholesterol derivatives; dyes and other colorants, perfumes, and ultraviolet light absorbers, chelating agents and foam boosters. The polymeric conditioning agents show little or no tendency to react with such additives.

The novel, hair conditioning shampoo compositions of this invention are prepared by dispersing the resin depositing, cationic polymer and the anionic surfactant in water with moderate agitation. When a homogeneous system is obtained, any optional ingredients may be added under appropriate conditions. For instance, the addition of a compound such as an amide may require heating the solution to ensure dispersion of the melted waxy material and the subsequent addition of a particular compound such as a perfume will require adequate cooling, prior thereto, to avoid its volatilization. Also it may be desired to slightly adjust the pH level.

The pH adjusting agent and quantity to be used should be chosen to ensure maximum efficiency of a shampoo composition which will not damage the hair or irritate the eyes or skin. A preferred pH range, for the solutions prepared according to this invention, is from 3.5-7.0. Since the initial pH level of the shampoo compositions herein is usually between 5.0 and 6.0, it is preferred that weak acids such as citric acid, acetic acid, phosphoric acid, and the like and weak bases such as the alkanolamines, e.g. triethanolamine, diethanolamine, etc. be used as pH adjusting agents. It is to be understood that the phrase "consisting essentially of" as used herein is not intended to exclude from the scope of this invention

compositions containing small amounts of the various additives that are discussed above and which are conventionally used in shampoo formulations.

5 The resulting shampoo formulations exhibit all of the characteristics required of such products. They are capable of thoroughly cleaning the hair with superior foaming and rinsability of lather while depositing thereon a film which conditions the hair. These conditioning properties are noticeable after only one shampooing but increase substantially over time upon repeated use of the shampoo formulations of this invention. 5

10 The films deposited on the hair fibres by the present, novel shampoo compositions possess good antistatic properties, adhere well to the hair, allow the hair to be readily recombed, do not become tacky when exposed to high humidities and are easily removed by conventional shampoos. In addition, it should be noted that the conditioning shampoos of this invention remain effective in cleaning the hair and imparting the desired manageability, wet and dry combing and, at times, curl retention properties thereto, when optional, conventional ingredients are incorporated therein. 10

15 The combined hair cleaning and conditioning procedure used in practicing this invention is essentially the same as that of a conventional shampoo technique. Ordinarily the hair is wetted, the shampoo preparation, as a concentrate, is applied and thoroughly massaged throughout the hair to ensure even distribution of the lather thus produced; the hair is then rinsed free of the lather, wiped partially dry, combed, and fixed in the desired configuration in which it is allowed to dry. The dried hair is then combed out into the desired set. Obviously, the practitioner may elect to repeat the cycle or otherwise vary from this technique without departing from the scope of this invention. 15

20 The invention will now be further illustrated by, but not intended to be limited by, the following examples. The quantities of all ingredients are given in parts, by weight, of the total formulation, unless specified otherwise. 20

#### Examples I - VI

25 These examples illustrate the preparation and effectiveness of a shampoo composition comprising various levels of a salt of an aminoalkyl ester of a ethylenically unsaturated carboxylic acid in combination with a variety of anionic surfactants. 25

30 Shampoo compositions were prepared using the ingredients and amounts shown in Table I. In each instance, the polyethylene glycol (PEG 400) monostearate was dissolved in water and the anionic surfactant added. When the mixture became homogeneous, the cationic polymer was slowly added with agitation, followed by addition of the lauric diethanolamide (a nonionic foam booster). After continued mixing, a uniform, clear shampoo solution resulted. 35

TABLE I

Ingredients	I	II	III	IV	V	VI
Phosphate salt of poly(aminoethyl acrylate hydroxypropyl acrylate) (18% aqueous solution) - Catrex supplied by National Starch and Chemical Corp.	5.60	11.20	5.60	11.20	5.60	11.20
Sodium lauryl ether sulfate (2 moles ethylene oxide) (25% aqueous solution) - Maprofix ES supplied by Onyx Chemical Co.	20.00	35.00	x	x	x	x
Triethanolamine lauryl sulfate (40% aqueous solution) - Maprofix TLS-500C supplied by Onyx Chemical Co.	x	x	15.00	20.00	x	x
Disodium salt of a sulfosuccinate half ester of an alkanolamide (30% aqueous solution) - Monamate OPA-30 supplied by Mona Industries.	x	x	x	x	45.00	45.00
Modified lauric diethanolamide - Monamid 716 supplied by Mona Industries.	2.00	2.00	2.00	2.00	2.00	2.00
PEG (400) Monostearate (nonionic foam booster, stabilizer, thickener)	3.00	3.00	3.00	3.00	3.00	3.00
Distilled water	69.40	48.80	74.40	63.80	44.40	38.80

Each of the shampoo compositions was then evaluated as follows:

- 5 Approximately 1/2 gram of shampoo was uniformly applied to wet swatches of virgin, brown European hair, each 10 inches in length and weighing approximately 2 grams. Each swatch was gently massaged for about 2 minutes to produce lather and the hair was then rinsed with warm tap water for one minute. The foregoing steps were repeated. Excess water was then squeezed out of the thoroughly rinsed swatches by running them between two fingers. Swatches were then found to be easily combed through while wet. Swatches were soft and silky and easy to comb when dry.

10 *Example VII*

Shampoo compositions according to the present invention were prepared using a plurality of anionic surfactants and adopted for use on normal, oil and dry hair as shown in Table II.

- 15 In each case, the Condanol (Registered Trade Mark) SBFA/3 was dissolved in water and the cationic polymer added with agitation. After the solution became homogenous, the remaining ingredients were added with agitation continuing until a uniform mixture was formed. After filtering, the shampoo formulations were evaluated as described in Examples I - VI and all three found to give superior results leaving the hair clean, and manageable with good body.

TABLE II

Ingredients	Normal Hair	Parts by Weight Oily Hair	Dry Hair
Distilled water	24.90	16.90	31.90
Fatty alcohol ether sulfosuccinate (40% aqueous solution) Condanol SBFA/3 supplied by Dutton & Reinisch Ltd.	40.00	40.00	40.00
Phosphate salt of poly(aminoethyl acrylate hydroxypropyl acrylate) (18% aqueous solution) Catrex supplied by National Starch and Chemical Corp.	5.60	5.60	5.60
Lanolin Derivative Emollient - Lanexol AWS supplied by Croda.	x	x	1.00
Sodium lauryl ether sulfate (2 moles ethylene oxide) (25% aqueous solution) - Maprofix ES supplied by Onyx Chemical Co.	10.00	15.00	5.00
Triethanolamine lauryl sulfate (40% aqueous solution) - Maprofix TLS-500C supplied by Onyx Chemical Co.	15.00	20.00	10.00
Polyoxyethylene (4) lauryl ether - Brij (Registered Trade Mark) 30 supplied by ICI.	2.00	1.00	3.00
Modified lauric diethanolamide - Monamid 716 supplied by Mona Industries.	2.00	1.00	3.00
Sodium Chloride	0.50	0.50	0.50
Dye, Perfume, Preservative	q.s.	q.s.	q.s.
10% Phosphoric acid	to pH 6-7	to pH 6-7	to pH 6-7

*Example VIII*

Shampoo compositions similar to those described in Example VII were prepared using the procedure disclosed therein and then evaluated in the manner described hereinbelow. The shampoo compositions are as follows:

TABLE III

	Ingredients	Amounts	
10	Distilled water	q.s. to 100%	10
	Monamate OPA-30	25.95	
	Catrex	0 to 7%	
	Maprofix ES	10.85	
	Maprofix TLS-500C	14.16	
15	Brij 30	1.89	15
	Monamid 716	2.36	
	NaCl	0.30	
	Fragrance	0.09	
	Tetrasodium EDTA (a chelating agent)	0.24	
20	Versene (Registered Trade Mark) 100 supplied by Dow		20
	Methyl-p-hydroxy benzoate (preservative)	0.09	
	Propyl-p-hydroxybenzoate (preservative)	0.01	

25 *Theory of test method:* 25

30 Hair is known to contain a number of "free" anionic (acidic) sites and "free" cationic (basic) sites which can bind chemical species of the opposite ionogenic class. It has been shown that the basic groups will readily and reproducibly combine with Orange II dye in a formic acid medium. The degree of combination is easily determined through measurement of Orange II depletion from a standard solution in contact with hair under controlled conditions. 30

35 It is further known that the deposition of a cationic polymer onto the hair increases the number of basic sites per unit of hair. This modification, therefore, adds to the dye combining capacity of the hair. The degree of cationic polymer pickup by the hair is determined by relating dye combining capacity of hair treated with the test material to hair treated with a control sample. 35

40 *Preparation of orange II stock solution:* 40  
The acid form of Orange II was prepared by acidifying a concentrated aqueous Orange II solution (p-(2-hydroxy-1-naphthylazo) benzene sulfonic acid/Pylam Products Inc.) with hydrochloric acid. The dye was then isolated from an aqueous - alcoholic solution by filtration, then dried. A stock solution of the acid Orange II was prepared in formic acid at a concentration of 2 mg acid Orange II per gram of reagent formic acid.

45 *Standard curve preparation:* 45  
A standard curve of optical density vs. dye concentration was prepared by first weighing aliquots of 0.10g, 0.20g, 0.30, 0.40g, and 0.50g. of stock solution into pretared 50 ml. volumetric flasks. Two milliliters of 0.20 M sodium acetate buffer (adjusted to pH 5.6 with acetic acid) were added and finally diluted to 50.00 ml with distilled water. Optical density of each was determined at 485 mμ with a Beckman DB spectrophotometer. 50

The standard curve was a straight line emanating from the origin, following the equation.

55  $C = 0.0024D$  55  
Where C = mmol of H<sup>+</sup> Orange II in test solution  
D = Optical density of test solution



The results obtained for each of the shampoo compositions are shown below and are compared with a commercially available conditioning shampoo.

5	Sample	Mean Dye Pickup (mmol/g. hair)	5
	Test shampoo with 0% Catrex	0.112	
	Test shampoo with 3% Catrex	0.125	
	Test shampoo with 5.7% Catrex	0.129	
10	Test shampoo with 7% Catrex	0.138	10
	Commercial Conditioning Shampoo (containing a cationic quaternized cellulosic polymer, an anionic and an amphoteric surfactant)	0.126	

15 15

*Hair preparation and exposure to test shampoo:*

Ten inch bleached blonde hair was separated into swatches of approximately 2 grams in weight. These were secured and bound at the root end with cotton thread and epoxy cement.

20 A swatch under test (8 per test sample) was wetted with distilled water and shampooed with approximately 0.05 g. of the test shampoo. Lather was formed and evenly distributed throughout the swatch. After a ten minute contact time, the swatch was rinsed thoroughly for one minute under 100°F. tap water. Excess water was squeezed out. Swatches were dried at 120°F. for 1 hour then equilibrated at 70°F./50% RH for 24 hours.

25 25

*Dye pickup and measurement*

Approximately one-half inch of each of the test swatches (0.10-0.15g. hair) were cut off the unbound end and weighed onto pretared 50 ml Erlenmeyer flasks. Twentyfive milliliters of stock dye solution were pipetted into each flask. Flasks were then stoppered and the hair was allowed to remain in contact with the dye solution for 16 hours. Robbins et al. (Textile Research Journal, 38 (11) 1968) reported that maximum pickup is achieved under these conditions in less than 2 hours.

30 A 0.2 g.-0.4 g. aliquot of each sample of "exhausted dye solution" was weighed into a pretared 50 ml volumetric flask. Two milliliters of the sodium acetate buffer solution were added and the samples were diluted with distilled water. Samples were mixed thoroughly and optical density was determined at 485 mμ with a Beckman DB spectrophotometer. The amount (mmol.) of dye sorbed by the hair sample can be determined by the equations.

$$DP = \frac{C_I - C_F}{W_h}$$

40 DP = dye bound by one gram hair  
C<sub>I</sub> = mmol. dye in 25 ml stock solution  
C<sub>F</sub> = mmol. dye in 25 ml exhausted dye solution  
W<sub>h</sub> = Weight hair sample (grams)

$$C_F = .0024D \times \frac{30.5}{WA}$$

45 D = Optical density test solution  
WA = Weight (grams) aliquot "exhausted dye solution"  
30.5 = Weight (grams) of 25 ml stock solution

*Example IX*

In accordance with the procedure described in Example I, shampoo compositions can be prepared using any of a variety of cationic polymers. Thus, shampoos which lather and rinse well and leave the hair manageable and full bodied may be prepared within the scope of the present invention using any of the representative polymers shown in Table IV.

TABLE IV

10	Polymers	Monomer proportions mole percent	10
	Phosphate salt of poly(aminoethyl)acrylate	-	
15	Hydrochloride salt of poly(aminoethyl acrylate/acrylamide)	50/50	15
	Phosphate salt of poly(aminoethyl acrylate/aminoethyl crotonate)	95/5	
20	Hydrochloride salt of poly(aminoethyl methacrylate)	100	20
	Phosphate salt of poly(2-aminopropyl acrylate/diethyl fumarate)	75/25	
25	Phosphate salt of poly(aminoethyl acrylate/ acrylamide/hydroxypropyl acrylate)	80/4/16	25
30	Phosphate salt of poly(aminoethyl acrylate/ acrylamide/hydroxypropyl acrylate)	75/15/10	30
	Phosphate salt of poly(aminoethyl acrylate/ diethyl fumarate)	85/15	
35	Phosphate salt of poly(aminoethyl maleate/ vinyl methyl ether)	50/50	35
	Phosphate salt of poly(N-ethyl aminoethyl methacrylate/dioctyl fumarate)	80/20	
40	Sulfuric acid salt of poly(aminoethyl acrylate/monomethyl maleate)	80/20	40
	Sulfuric acid salt of poly(N-methyl amino- ethyl acrylate/ethyl acrylate)	70/30	
45	Phosphate salt of poly(aminoethyl methacrylate/ dodecyl methacrylate)	80/20	45
50	Hydrochloride salt of poly(aminoethyl acrylate/ vinyl acetate)	80/20	50

## WHAT WE CLAIM IS:-

1. An aqueous conditioning shampoo free of amphoteric surfactants and consisting essentially of water and:
  - i) from 0.1 to 10.0%, based on the total weight of the solution, of a cationic polymer, said polymer having a molecular weight in the range 5,000 to 250,000 and being an acid addition salt of polymer containing aminoalkyl ester groups on the polymer backbone;
  - ii) from 5.0 to 30.0% by weight active solids, based on the weight of the solution, of one or more anionic surfactants selected from: fatty alcohol sulfates and ether sulfates, alkylaryl sulfonates, alkali metal alkyl sulfosuccinates, fatty alcohol ether sulfosuccinates, alkali metal sulfosuccinate half-esters of an alkanolamide, and alkali metal alkylaryl polyethoxy-ethanol sulfates and sulfonates; and
  - iii) from 0 to 10.0% by weight active solids, based on the weight of the solution, of one or more nonionic surfactants.

2. A shampoo according to claim 1, wherein the cationic polymer is a mineral acid addition salt of an amino ( $C_1-C_6$ ) alkyl ester of

- i) a homopolymer of an unsaturated carboxylic acid of from 3 - 5 carbon atoms;
- ii) a copolymer of two or more such acids, or

5 iii) a copolymer of one or more such acids with up to 50 mole per cent of one or more comonomers selected from: vinyl acetate, vinyl propionate, vinyl methyl ether, vinyl ethyl ether,  $C_1-C_8$  alkyl halfesters of maleic and fumaric acids, amides of acrylic and methacrylic acid, and  $C_1-C_{18}$  alkyl and  $C_2-C_4$  hydroxyalkyl esters of acrylic and methacrylic acid.

10 3. A shampoo according to claim 2, wherein the cationic polymer is a phosphate salt of poly(aminoethyl acrylate), a poly(aminoethyl acrylate hydroxypropyl acrylate) or a terpolymer of a) an aminoalkyl ester of an ethylenically unsaturated carboxylic acid, b) an amide of an ethylenically unsaturated carboxylic acid, and c) a hydroxyalkyl ester of an ethylenically unsaturated carboxylic acid, the said cationic polymer having a molecular weight in the range 25,000 to 100,000.

15 4. A shampoo according to any one of the preceding claims, wherein the anionic surfactant is

sodium lauryl sulfate,  
sodium lauryl ether sulfate  
sodium isopropylbenzene sulfonate,  
20 triethanolamine lauryl sulfate  
potassium isopropylbenzene sulfonate,  
isopropyl naphthalene sulfonate,  
sodium octenyl sulfosuccinate,  
sodium N-methyl-N-palmitoyl taurate,  
25 sodium oleyl isethionate, or  
sodium t-octyl phenoxy (ethoxy)<sub>1.5</sub> ethyl sulfate or sulfonate.

5. A shampoo according to any one of the preceding claims, which contains from 0.5 - 2.0% by weight of component i), from 10 - 20 % by weight of component ii) active solids basis, and from 2.0 to 8.0 % by weight of component iii) active solids basis.

30 6. A shampoo according to claim 5, wherein the nonionic surfactant is a polyoxyalkylene alkyl ether or an alkylene oxide/fatty acid condensate.

7. A composition according to claim 1, substantially as hereinbefore described in any one of the foregoing examples.

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